Characterization of the Forms of Arsenic in Soil/Sediment to Evaluate Mobility and Treatment

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The chemical compositions or forms of arsenic in solid materials are typically evaluated using indirect methods such as sequential leaching procedures or elemental analyses. As opposed to indirect methods, electronmicroprobe (EM) techniques can determine the form, associations and morphology of individual particles of arsenic-containing materials. This information is extremely beneficial in evaluating the mobility and treatment of arsenic in solid materials.

Case Study No. One – Arsenical Pesticide Manufacturing Site

Waste materials from the manufacture of sulfuric acid and lead arsenate were disposed at this site. Subsequent disposal of animal by-products and hides caused reducing conditions which mobilized the arsenic resulting in arsenic(3+) and organic (methylated) arsenic in ground water. The contaminated ground water is confined to the outwash deposits of a buried valley aquifer and discharges to a surface water pond. Even though elevated concentrations of arsenic enter the pond from the ground water (490 µg/L) and pore water concentrations in the pond sediments are high (1,700 µg/L), concentrations of arsenic in water discharging from the pond are very low (<5 – 12.2 µg/L). EM studies of the pond sediments indicated that the arsenic had been removed by adsorption to natural iron-containing minerals (eg, biotite). The adsorption capacity of the sediments was measured to be 3,350 mg As/Kg of sediment.

Case Study No. Two – Wood Treating Site

At this site, wood was treated with zinc meta-arsenite ($ZnAs_2O_4$) and resulted in contaminated soil. Batch leaching studies were performed to determine the mobility of the arsenic in the soil. Results indicated "reverse" isotherms with lower adsorbed concentrations in the soil at higher water concentrations. EM studies of the soil revealed arsenic-containing (eg, 0.5 percent) iron oxyhydroxide solid phases. In addition, small particles of arsenic oxide (63 percent arsenic) were identified. Overall, the arsenic is present as arsenic oxide, in solid-solution with iron oxyhydroxide and adsorbed to iron containing minerals. The "reverse" isotherms are caused by dissolution of arsenic phases followed by adsorption onto the iron-containing minerals.

Case Study No. Three – Smelter Site

During the smelting of mineral concentrates to produce lead, zinc and other metals, a variety of waste materials were produced including calcine and bag house dust. These wastes and the associated contaminated soil contained large concentrations of arsenic (up to 20,900 mg/Kg). One alternative to treat the contaminated soil and solid waste was through solidification/stabilization (S/S) techniques. EM analyses were used to identify the form of the arsenic in the original waste materials and contaminated soil and in the treated materials from the S/S processes. The evaluations were used to determine the type and quantity of S/S agent to use and to determine the effectiveness of the treatment process. The calcine waste contained arsenic in the form of arsenopyrite, scorodite and arsenic-bearing oxyhydroxides. Due to the potential instability of scorodite at elevated pH values (caused by the cement S/S agent), ferrous sulfate was added to the mixture. The iron (2+) assisted in removing any arsenic leached from the solidified waste by coprecipitation with iron oxyhydroxides. EM studies indicated this process was effective with abundant iron oxyhydroxides present with up to 0.7 percent arsenic in the solidified materials.

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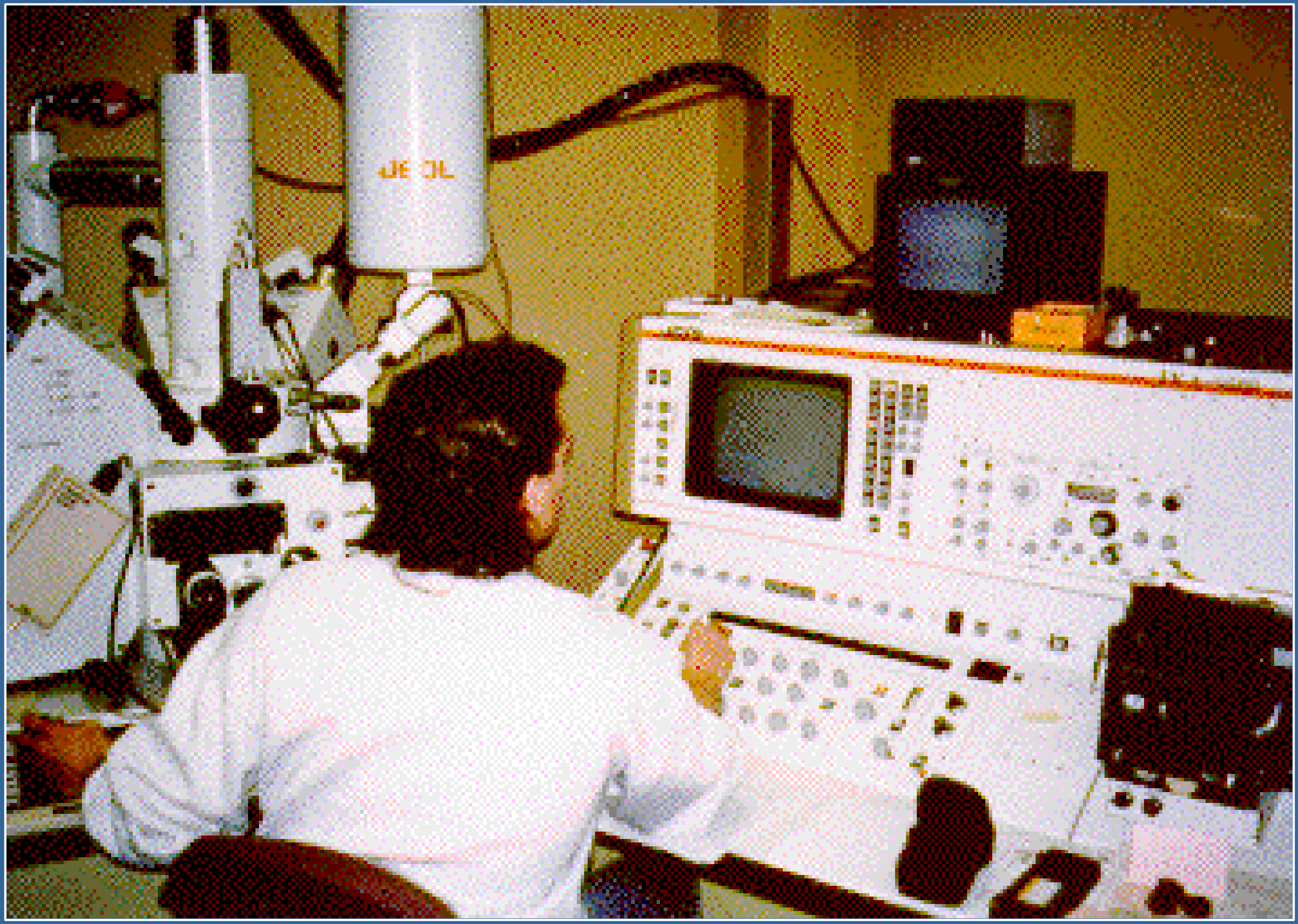
Methods to Characterize Arsenic in Solid Phases

- Elemental Analyses
- XRD
- Sequential Leaching Techniques
- X-Ray Photoelectron Spectroscopy
- EXAFS/ESCA/XANES
- Electron Microprobe

Electron Microprobe (EM)

- Advantages
  - direct observation of morphology
  - direct analysis of associations, rims
  - individual particles
  - quantitative determination
  - chemical formula
- Disadvantages
  - time
  - cost
  - concentration limited
  - cannot quantify hydrogen
  - two dimensional
  - limited sample size

Electron Microscope

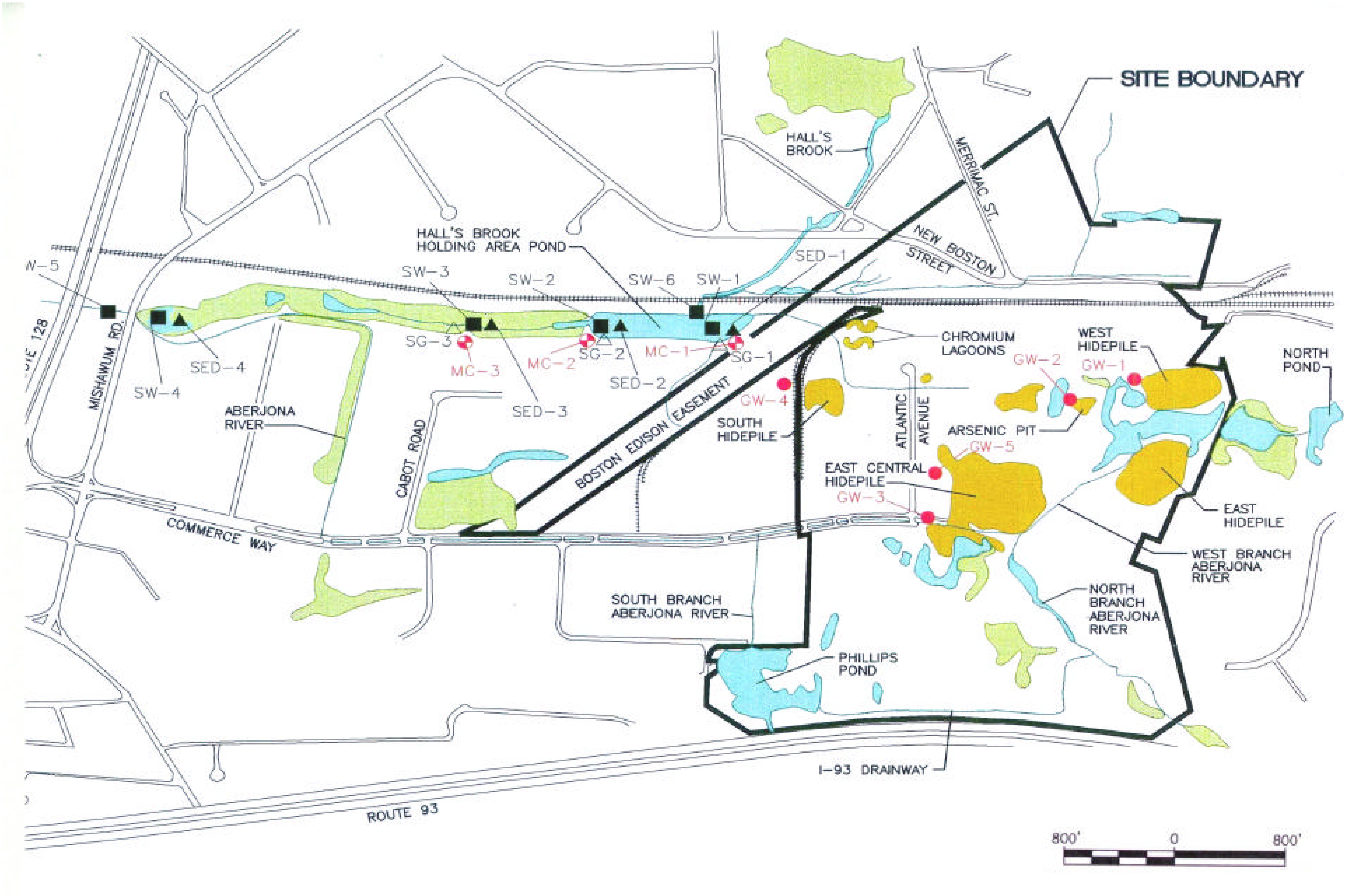


Three Case Studies

- Arsenical Pesticide Manufacturing Site
- Wood Treating Site
- Smelting Site

Arsenical Pesticide Monitoring Site
Industri-Plex Site
Woburn, Massachusetts

- **Used EM to Evaluate**
  - Mechanisms for Removal of Arsenic from Groundwater
  - Mobility of Arsenic in Surface Water/ Sediments



SITE BOUNDARY
HALL'S BROOK
MERRIMAC ST.
NEW BOSTON STREET
HALL'S BROOK HOLDING AREA POND
SED-1
SW-3
SW-2
SW-6
SW-1
W-5
SG-3
SG-2
SG-1
MC-3
MC-2
MC-1
SED-4
SED-2
SED-3
SW-4
MISHAWUM RD.
ABERJONA RIVER
CABOT ROAD
BOSTON EDISON EASEMENT
CHROMIUM LAGOONS
WEST HIDEPILE
GW-1
GW-2
GW-4
GW-5
GW-3
NORTH POND
SOUTH HIDEPILE
ATLANTIC AVENUE
ARSENIC PIT
EAST CENTRAL HIDEPILE
EAST HIDEPILE
WEST BRANCH ABERJONA RIVER
COMMERCE WAY
SOUTH BRANCH ABERJONA RIVER
NORTH BRANCH ABERJONA RIVER
PHILLIPS POND
I-93 DRAINWAY
ROUTE 93
800'
0
800'

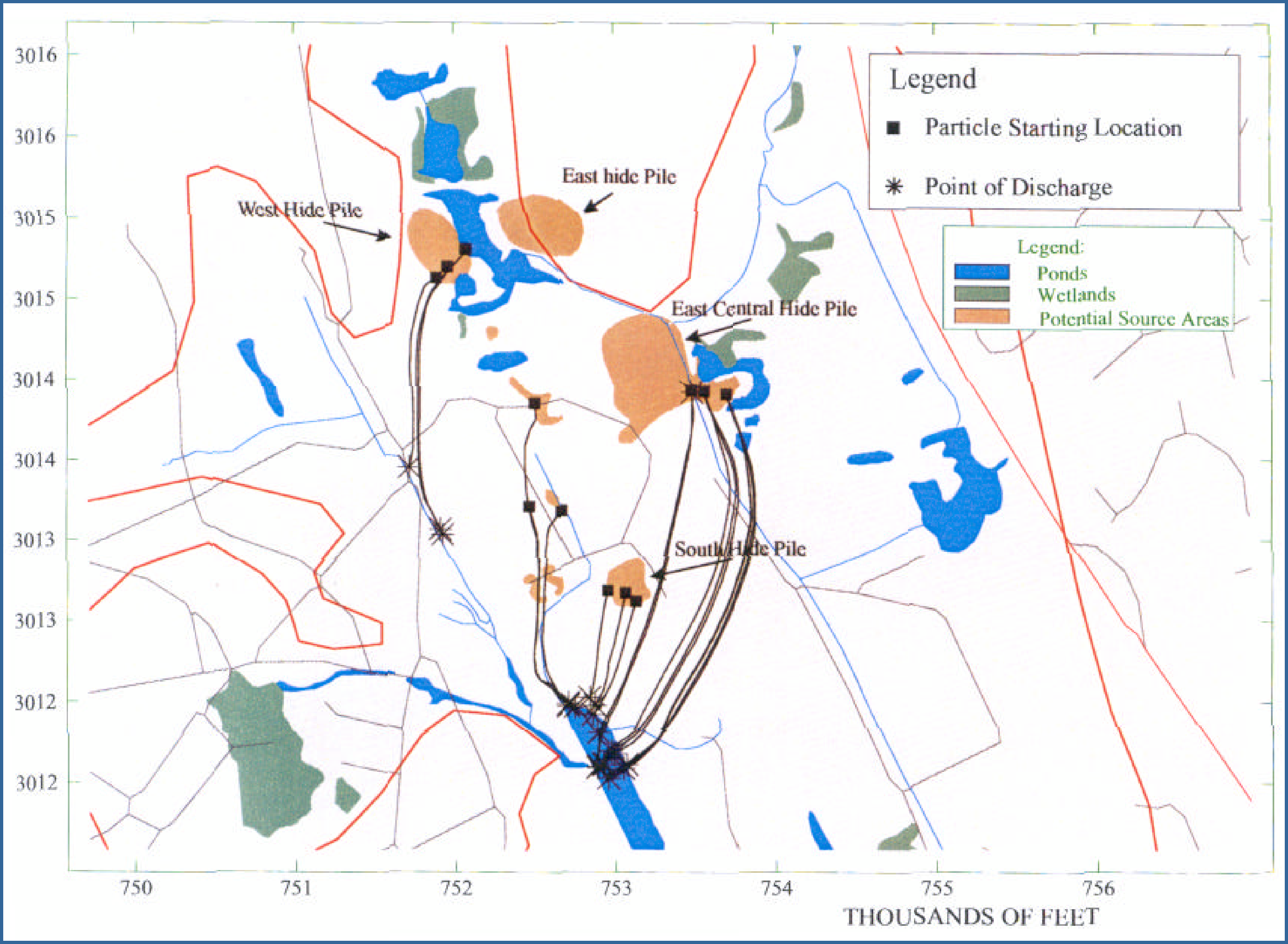
Waste Disposal

- Lead Arsenate Manufacturer
  - 1863 - 1929
- Sulfuric Acid Manufacturer
  - 1853 - 1929
- Subsequent Disposal of Animal Byproducts and Hides
  - 1934 - 1968

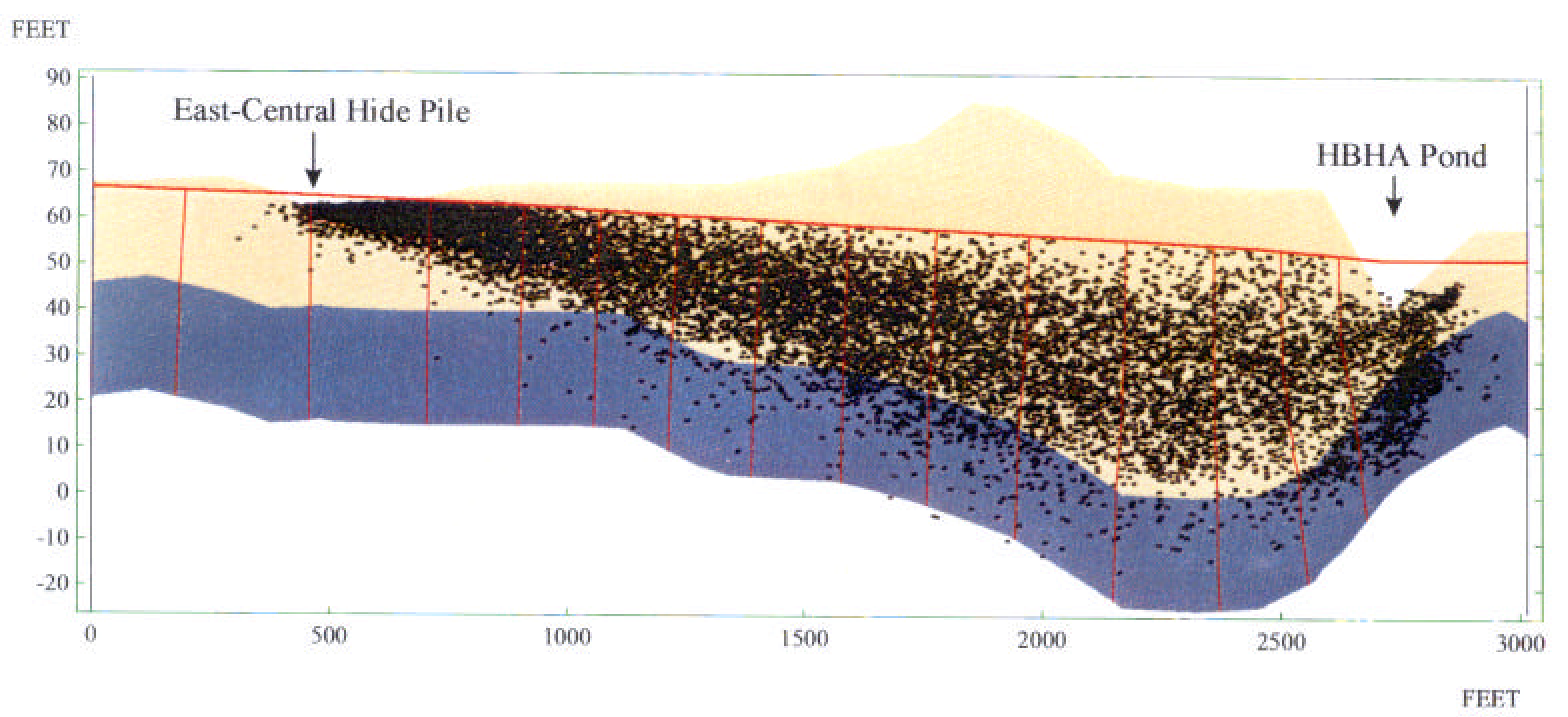
Groundwater Chemistry

- Source Area
  - As (III): 530 µg/L
  - As (V): 620 µg/L
  - As (organic): 600 µg/L
  - TOC, Sulfate, Bicarbonate Fe(2+), ammonium, pH, Eh
- Near HBHA Pond
  - As (III): 52 µg/L
  - As (V): 470 µg/L
- Pore Water
  - As (III): 1,100 µg/L
  - As (V): 610 µg/L
- Surface Water
  - As (total) dissolved: <5 - 12.2 µg/L

Groundwater Hydrogeology



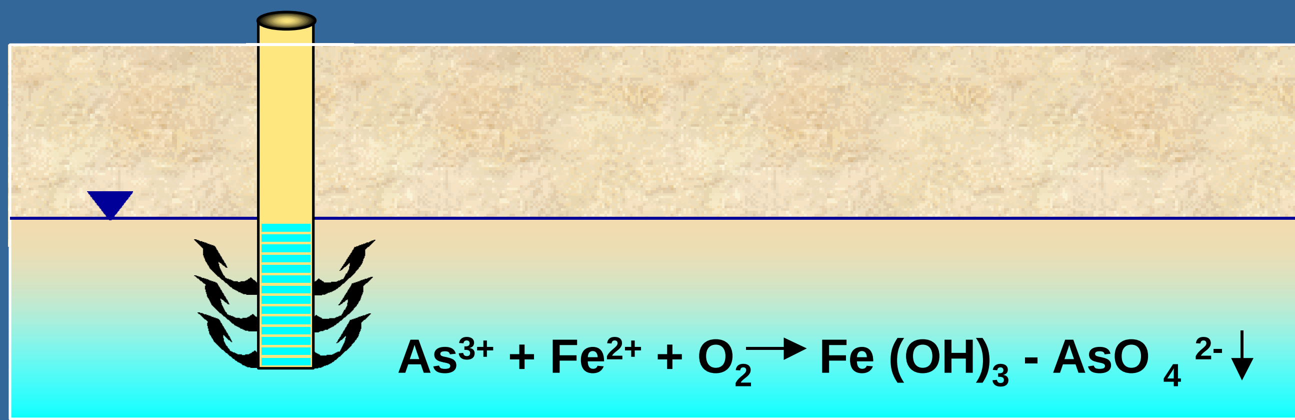
Groundwater Hydrogeology

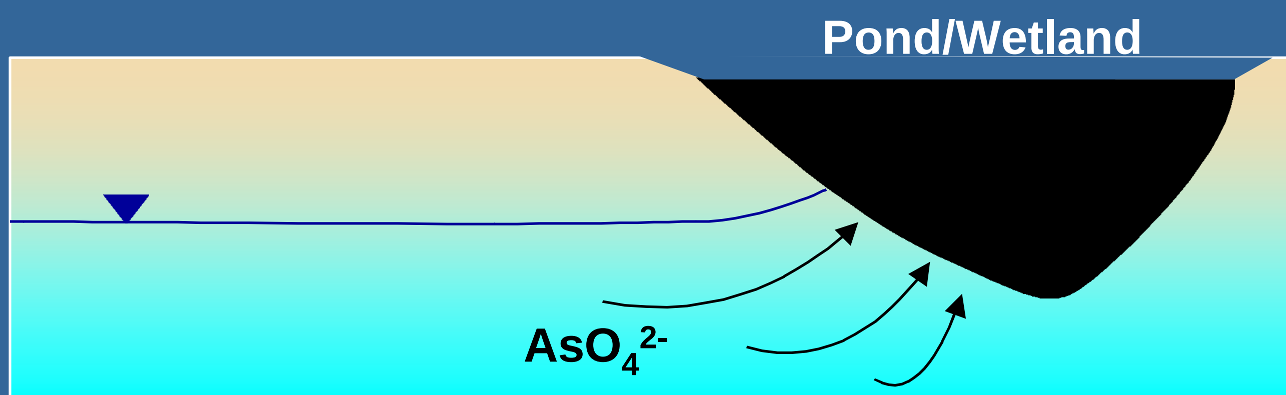


Sediment Chemistry

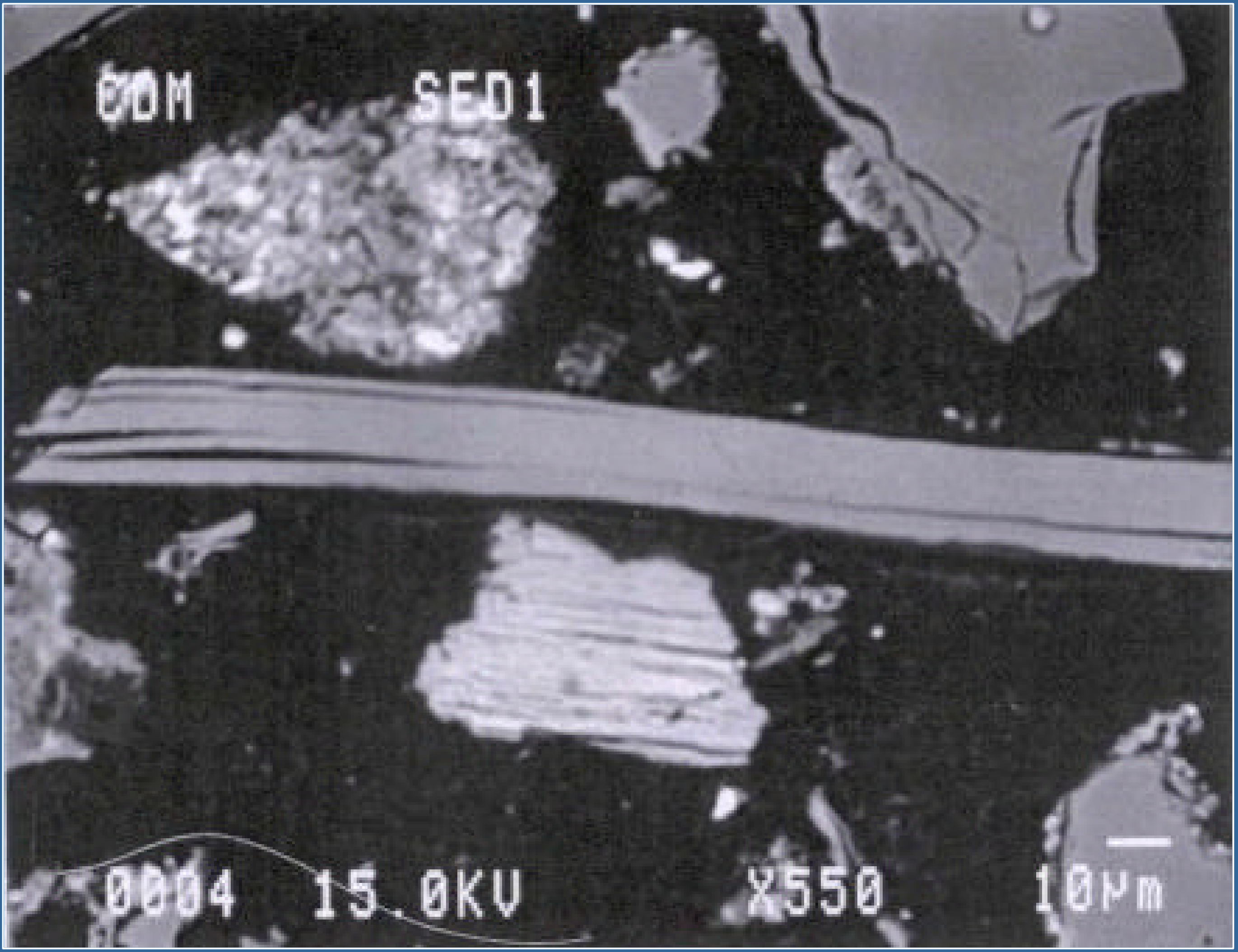
- As: 1390 - 9,830 mg/kg
- Variable with Location/Depth
- Sequential Leaching
  - ionic 1.5 mg/kg
  - manganese oxide 73 mg/kg
  - organic 26 mg/kg
  - poorly crystalline oxides of Fe, Al, Mn 6,500 mg/kg

Removal Mechanisms

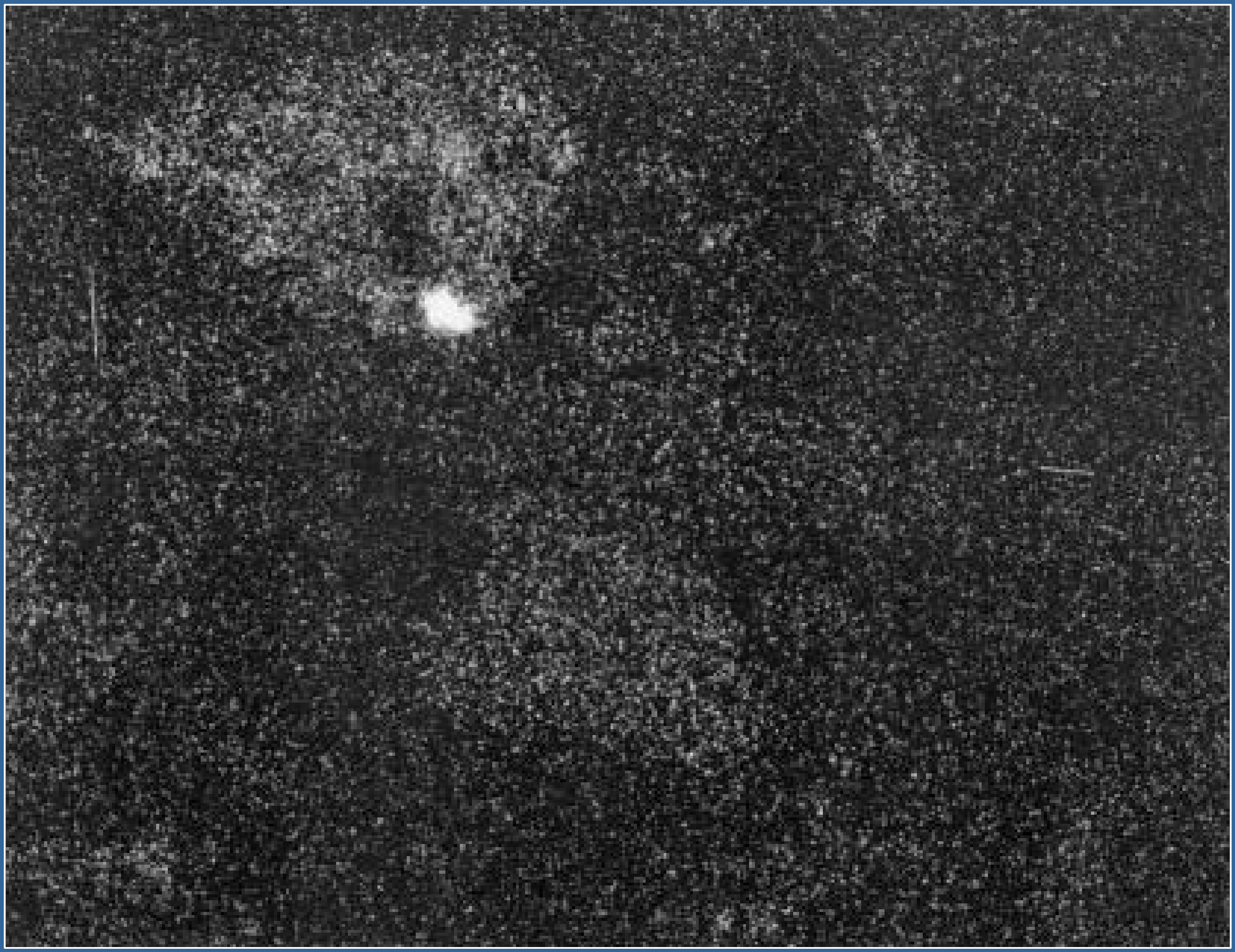




Sediment Sample

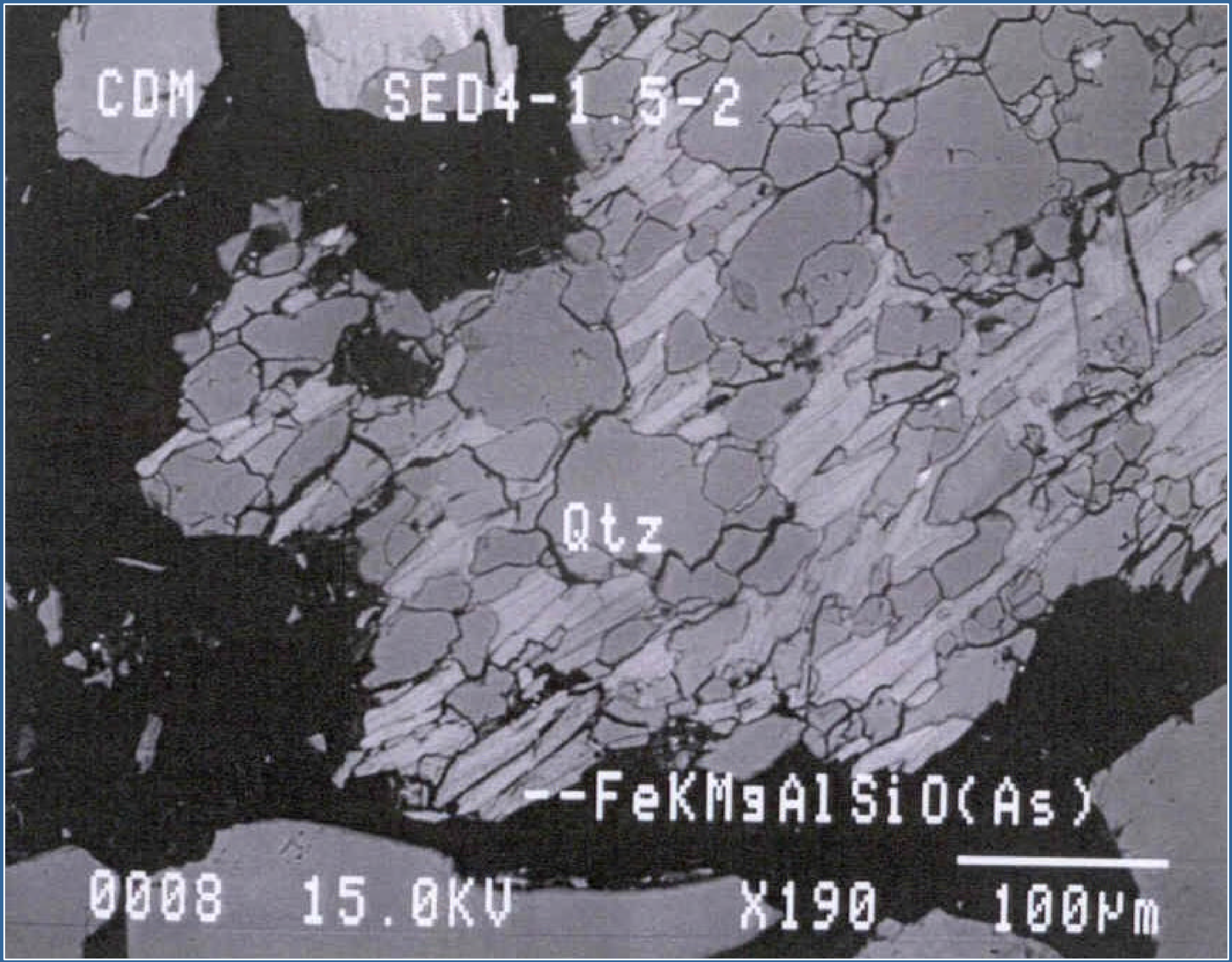


Arsenic Concentration Dot Map

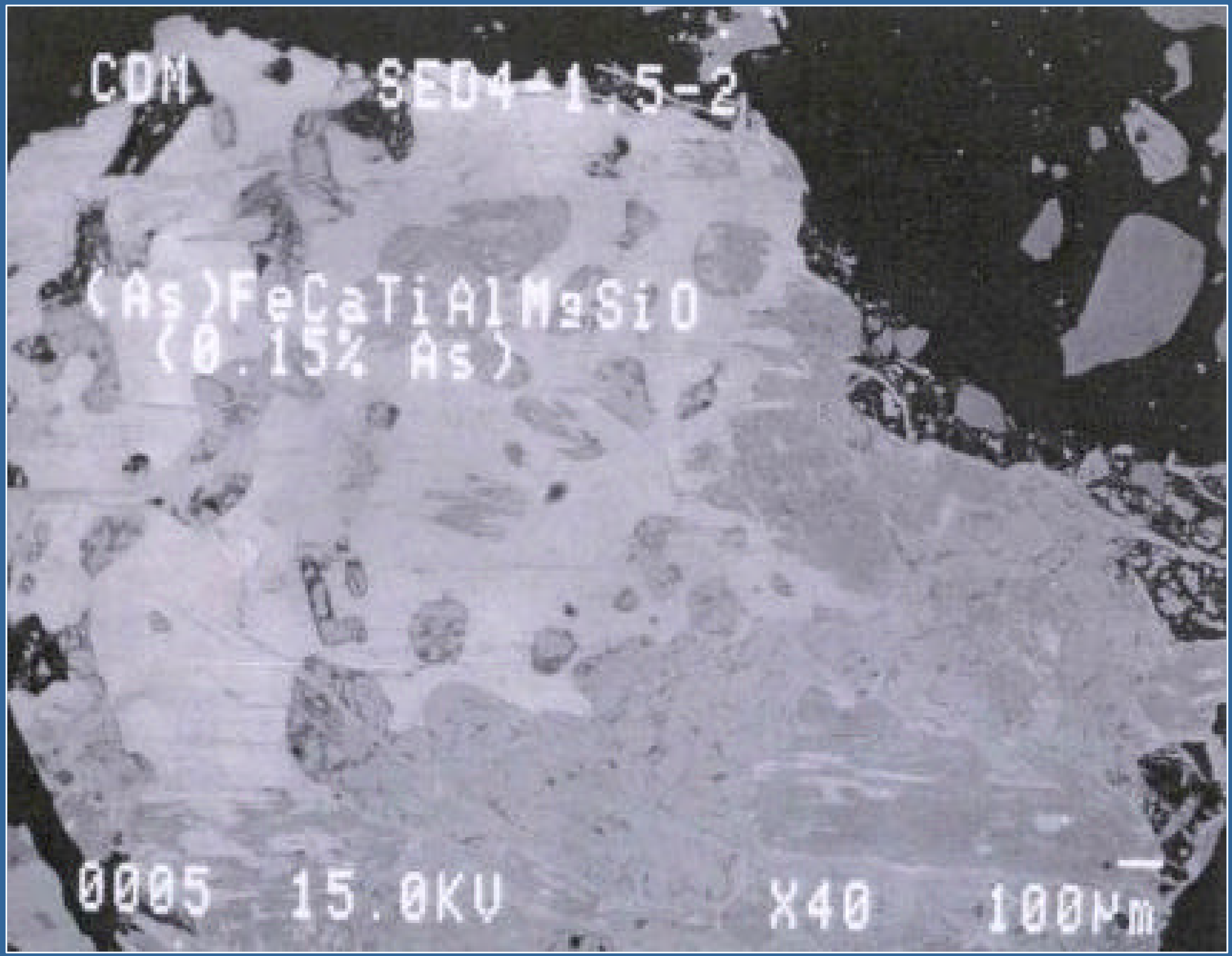


Arsenic Containing Biotite

Biotite and Quartz

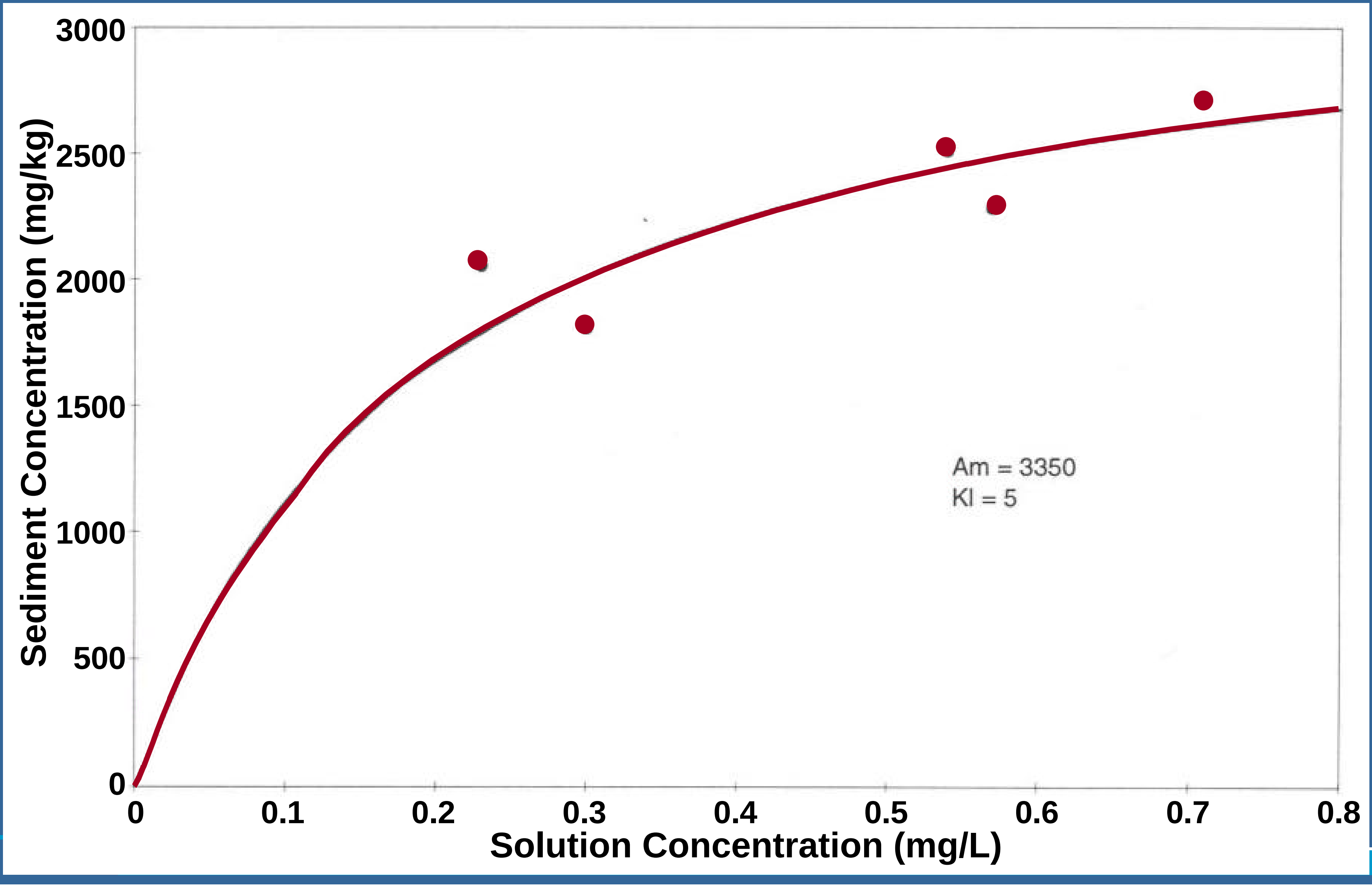


Arsenic Containing Amphibole/Pyroxene



Arsenic Isotherm

Pond Sediment (Am = 3350 mg/kg)



Long-Term Attenuation Capacity

Groundwater Inflows:	0.48 cfs
As Concentration:	120 µg/L
Remaining Adsorption Capacity:	1,960 mg/kg
Sediment Volume:	7,400 m^3
Life Time:	~ 300 yrs

Wood Treating Site
Jacksonville Electric Authority
Jacksonville, Florida

- **Assessment of Arsenic Mobility**
  - **groundwater modeling**
  - **risk assessment**
- **Batch Desorption Studies**
- **EM**

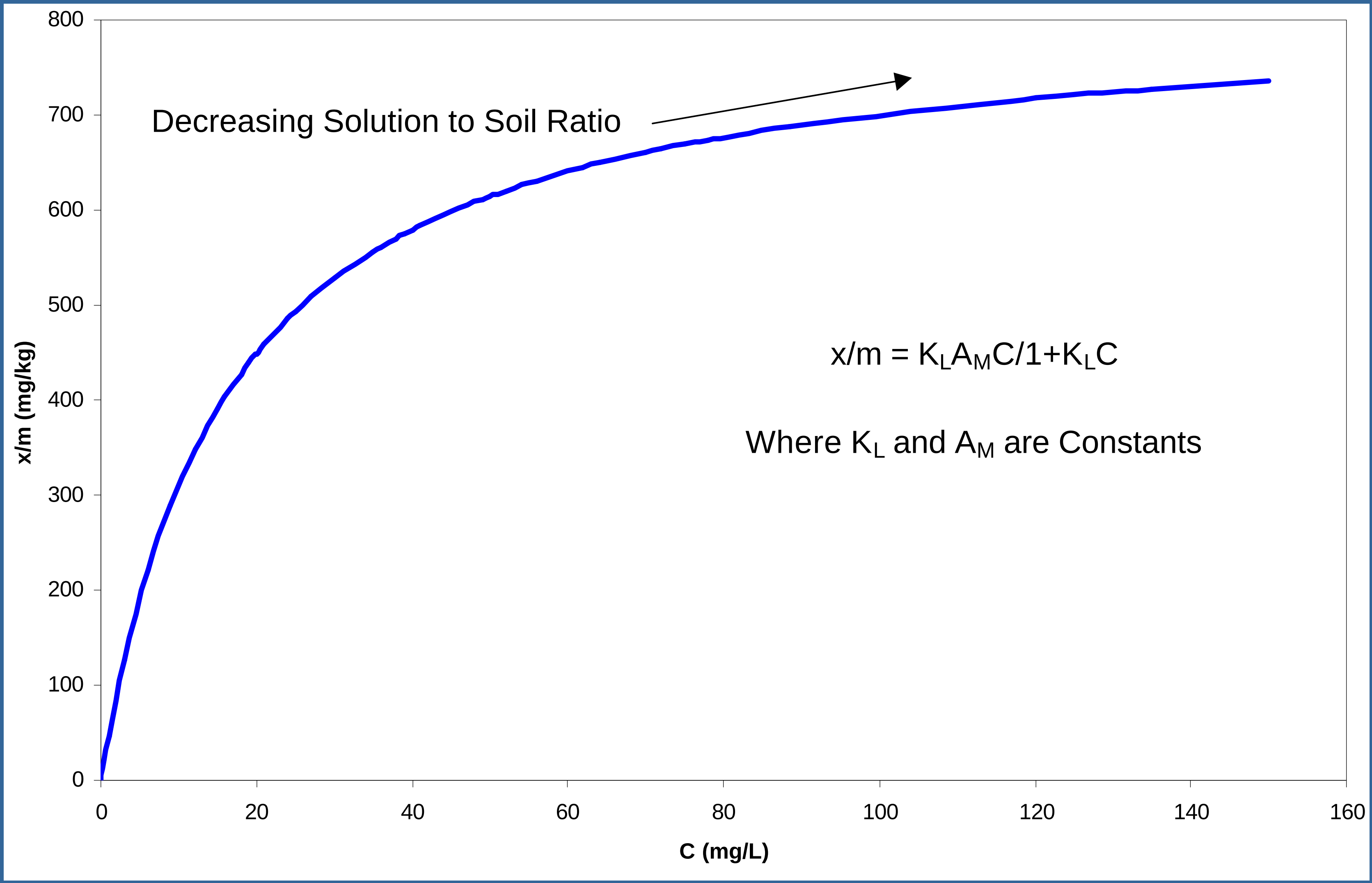
Site Description

- Former Wood Treating Facility
- Site Soils Contaminated with Arsenic and PAHs
  - Zinc Meta-arsenite (As_2O_4Zn)
  - Creosote

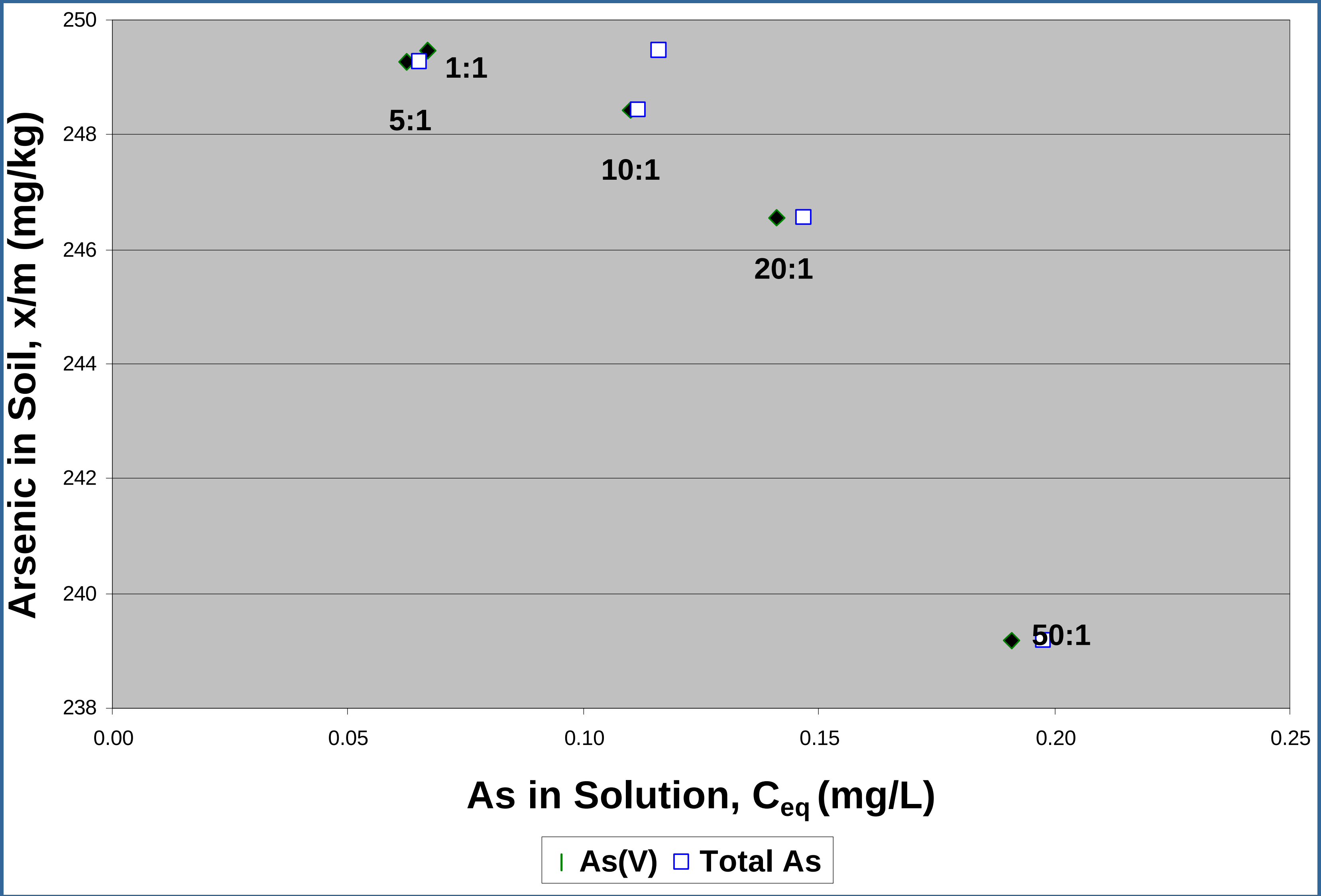
Batch Testing

- Synthetic rain water (SPLP) was used to simulate infiltration
- Five ratios (solution:soil)
  - 1:1, 5:1, 10:1, 20:1, 50:1
- Agitation for 72 hours
- Filter Solution through 0.45 µm membrane

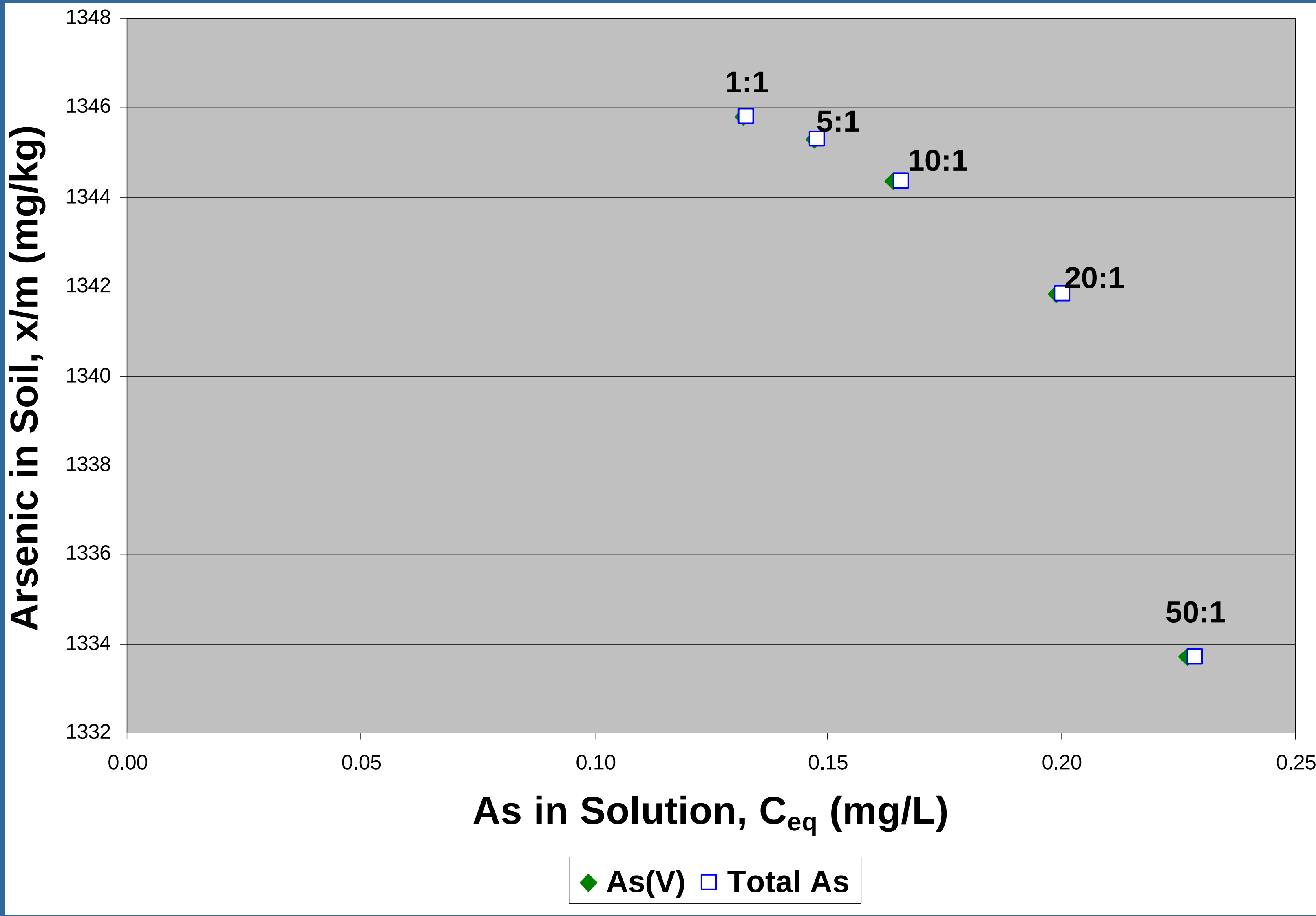
Typical Isotherm



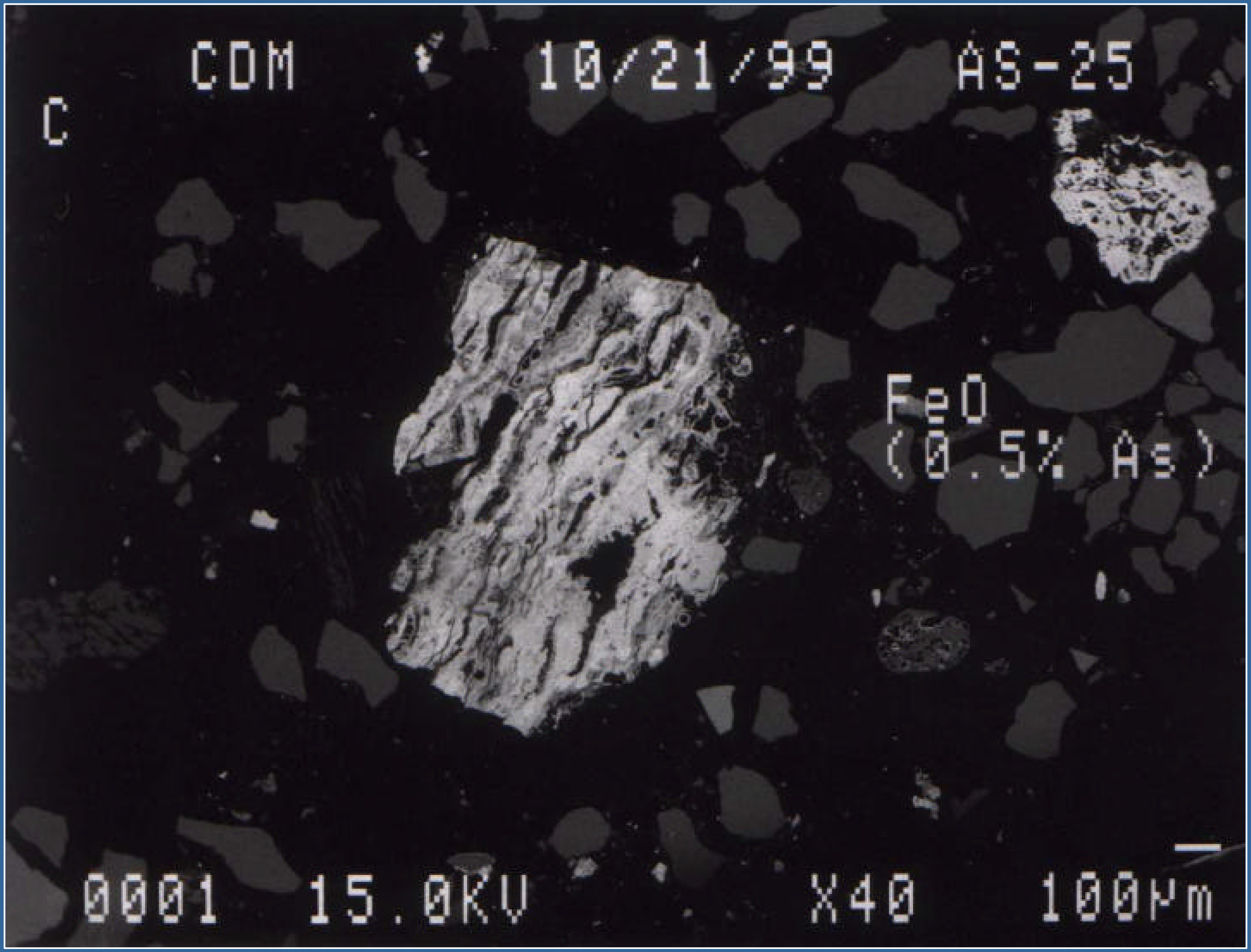
Isotherm - Soil Sample As-22



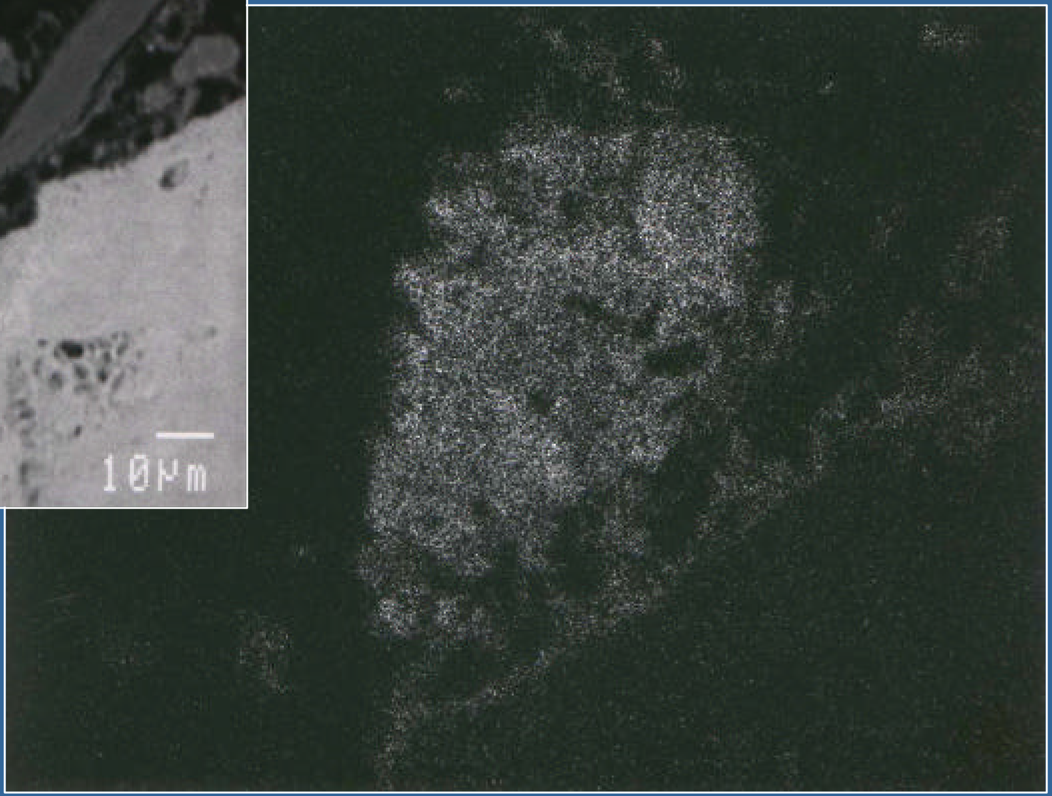
Isotherm - Soil Sample As-25



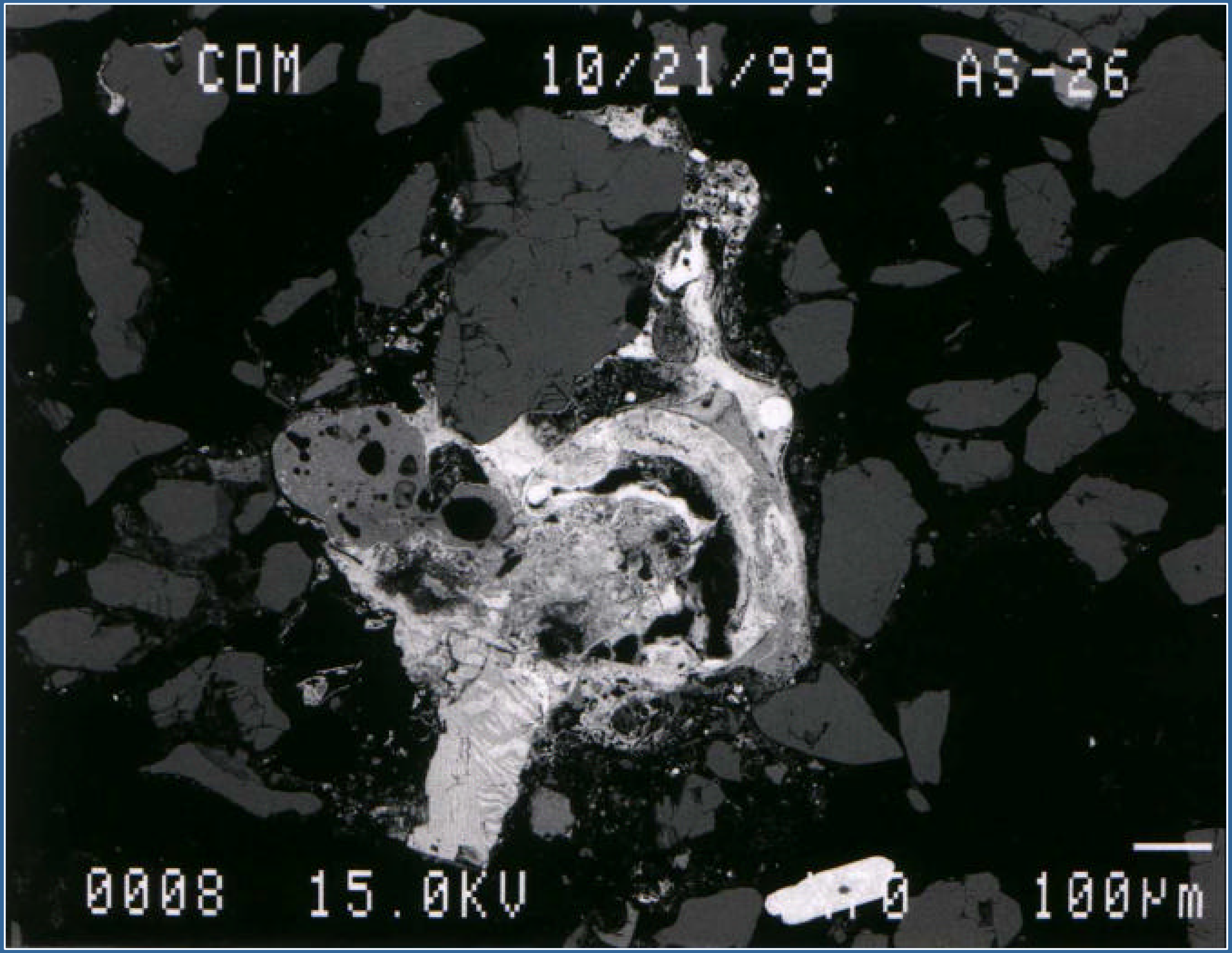
Sample As-25 - Iron Oxyhydroxide



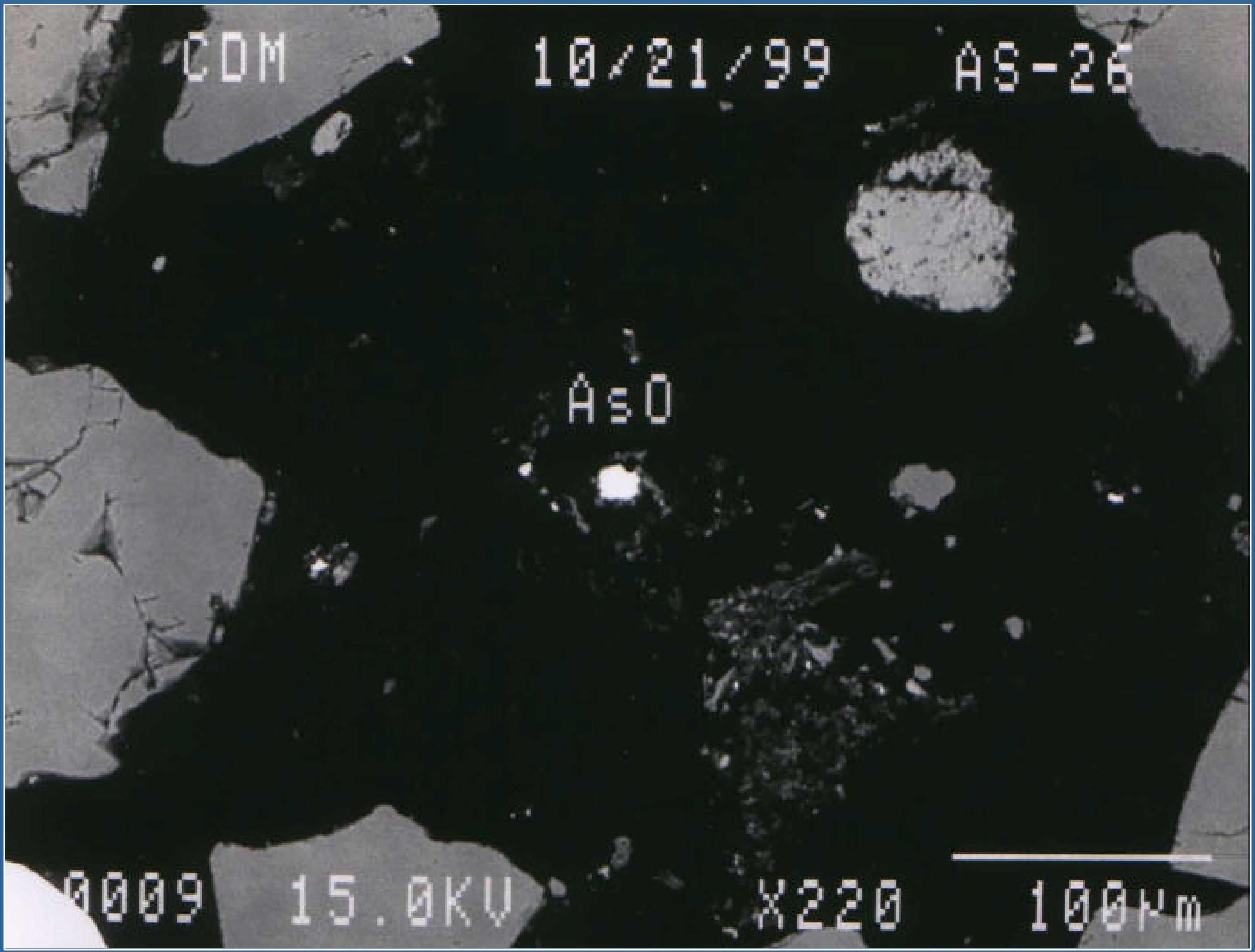
Sample As-25 - Iron Oxyhydroxide Dot Map



Sample As-26 - Iron Oxyhydroxide Cementing Quartz



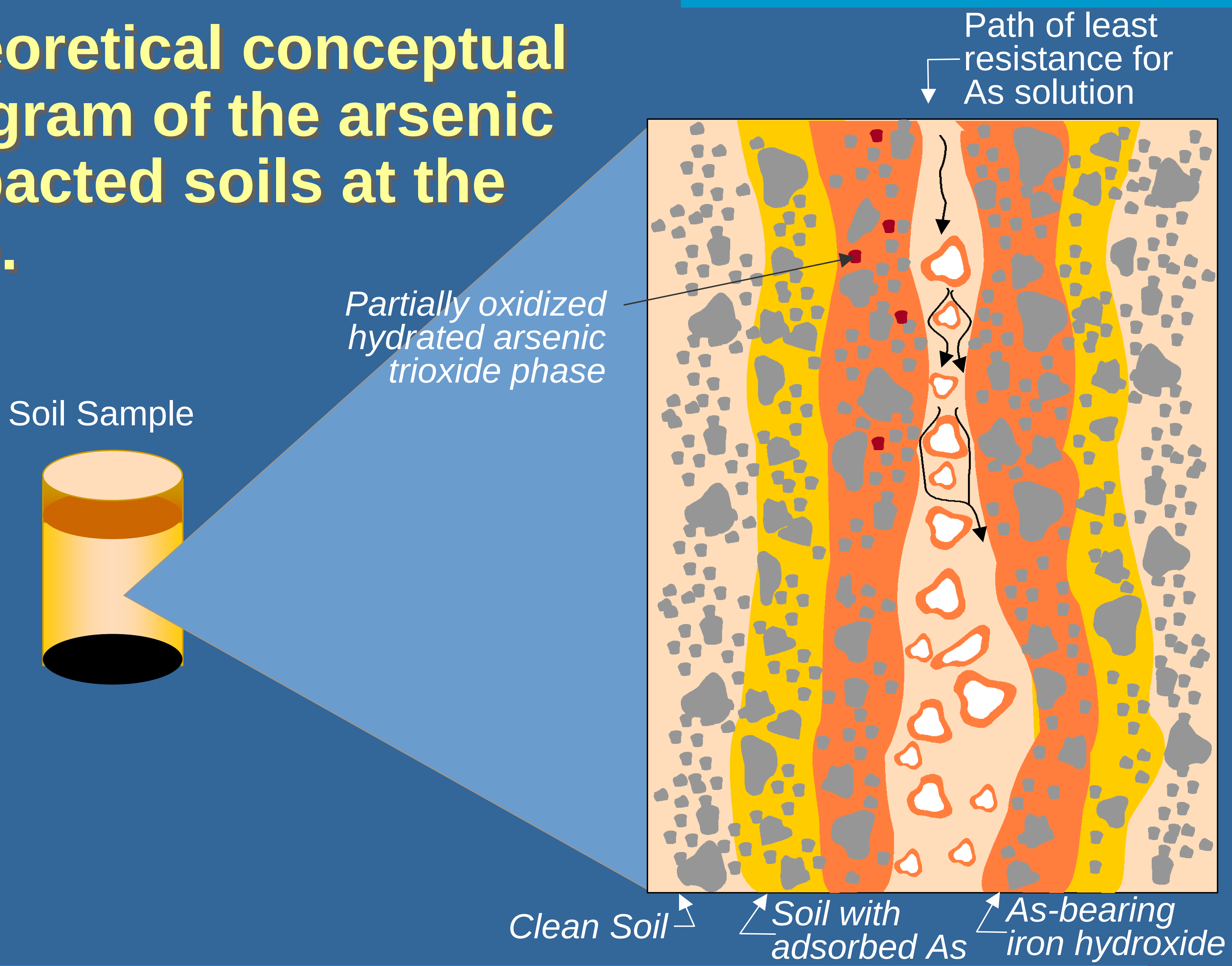
Sample As-26 - Arsenic Oxide Grain (63% Arsenic)



Arsenic Oxide Phases

Phase	Formula	As Valence	% Arsenic
Arsenic Trioxide	As_2O_3	+3	75.7%
Arsenous Acid	H_3AsO3	+3	59.5%
Arsenic Pentoxide	As_2O_5	+5	65.2%
Meta-Arsenic Acid	$(OH)AsO_2$	+5	60.4%
Ortho-Arsenic Acid	H_3AsO_4 1/2 H_2O	+5	49.6%
Pyro-Arsenic Acid	$H_4As_2O_7$	+5	56.4%

Theoretical conceptual diagram of the arsenic impacted soils at the site.



Conclusions

- Samples were probably not completely homogenized
- As is present as arsenic oxide, in solid-solution with iron oxyhydroxide, and adsorbed
- The “reverse” isotherms are caused by dissolution of As phases followed by adsorption

Smelter Site
Midvale Slag Site
Midvale, Utah

- Used EM to:
  - evaluate forms of arsenic in solid wastes
  - design solidification tests (agents, ratios, etc.)
  - evaluate effectiveness

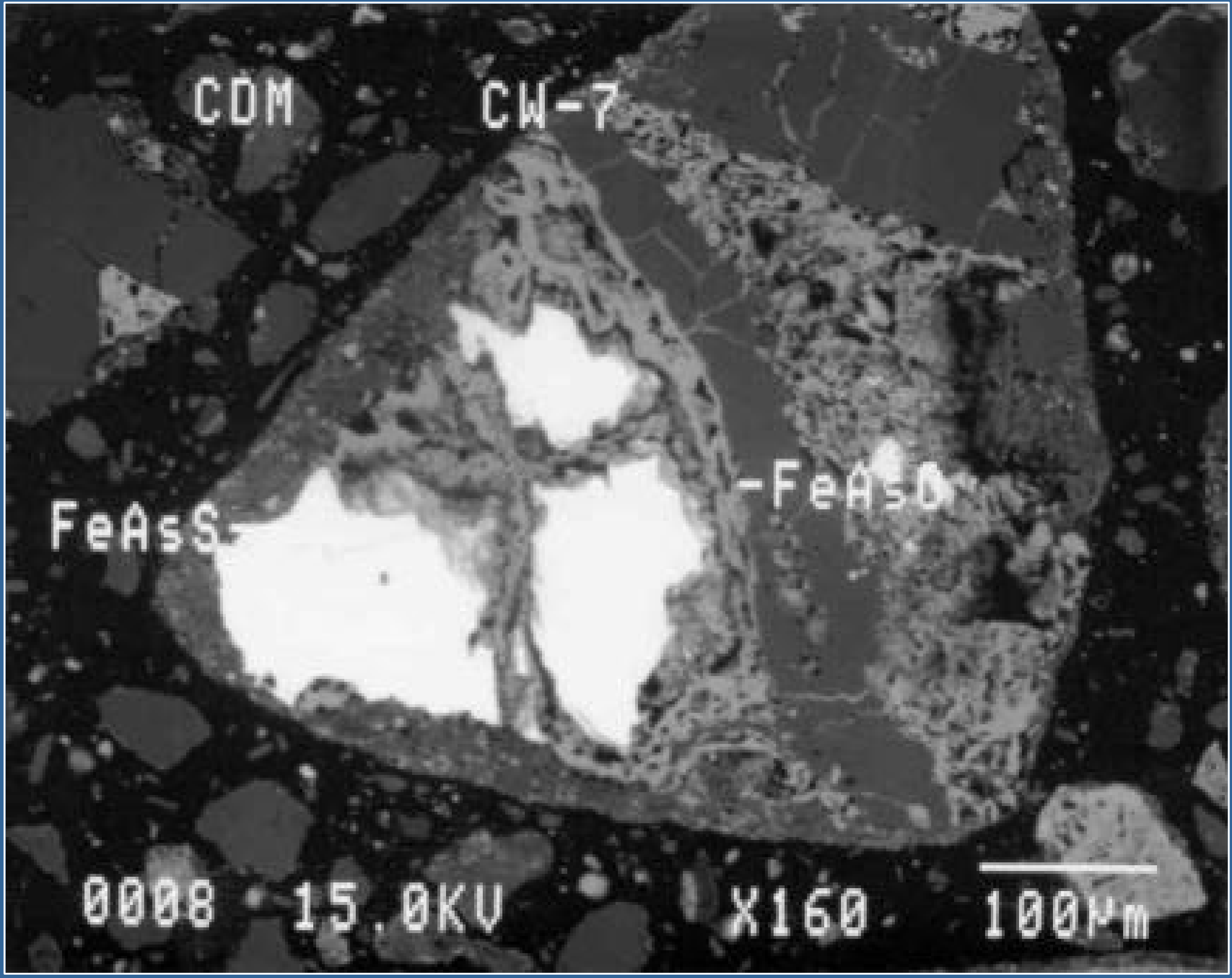
Waste Disposal

- Smelting and refining: 1871 - 1978
- Calcine Waste - roasted arsenopyrite ore
- Baghouse Dust
- Slag
- Bricks, Arsenic Trioxide

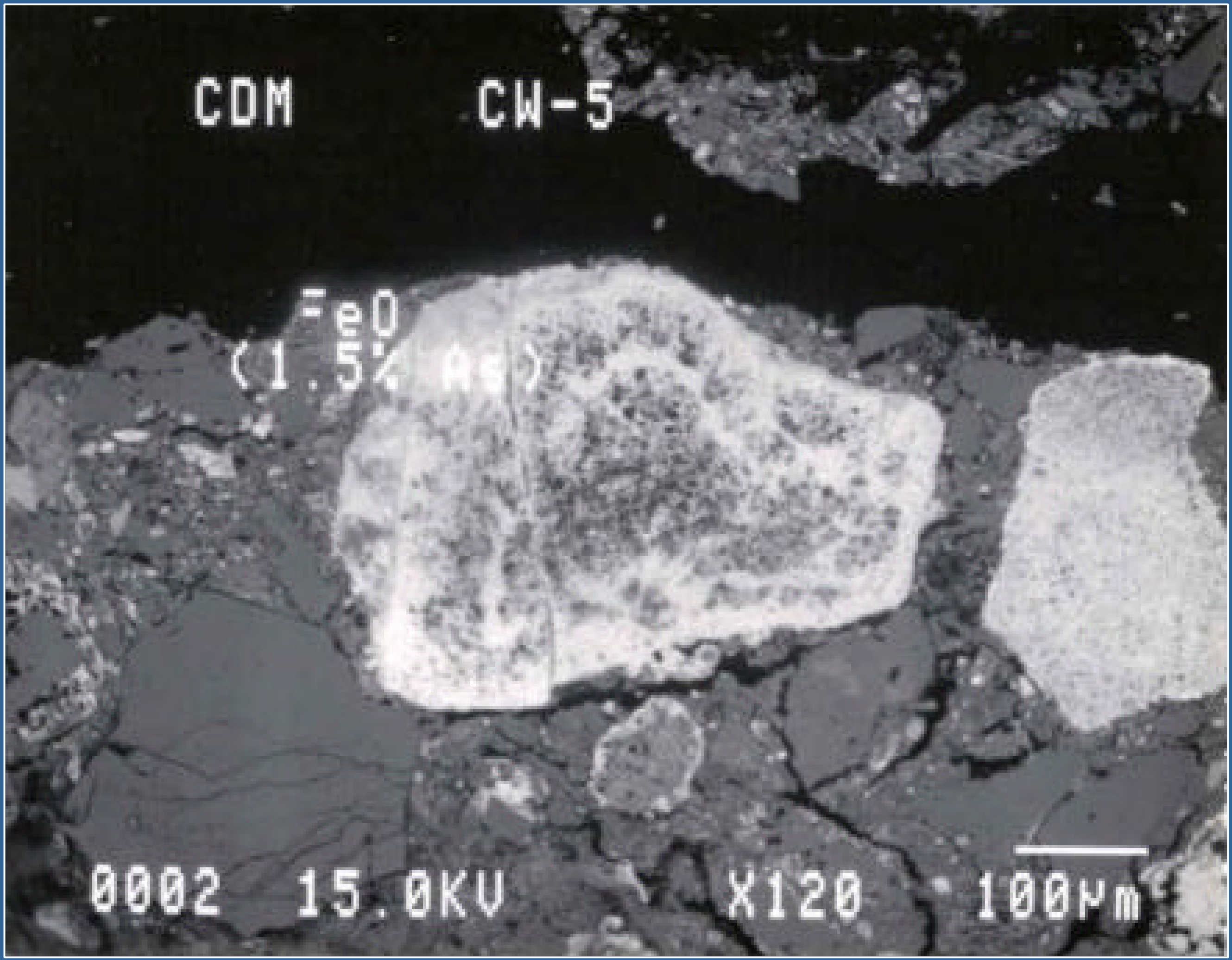
Calcine Waste

As	19,000 mg/kg
Fe	195,000 mg/kg
Pb	11,000 mg/kg
Zn	4,500 mg/kg
Sb	1,100 mg/kg

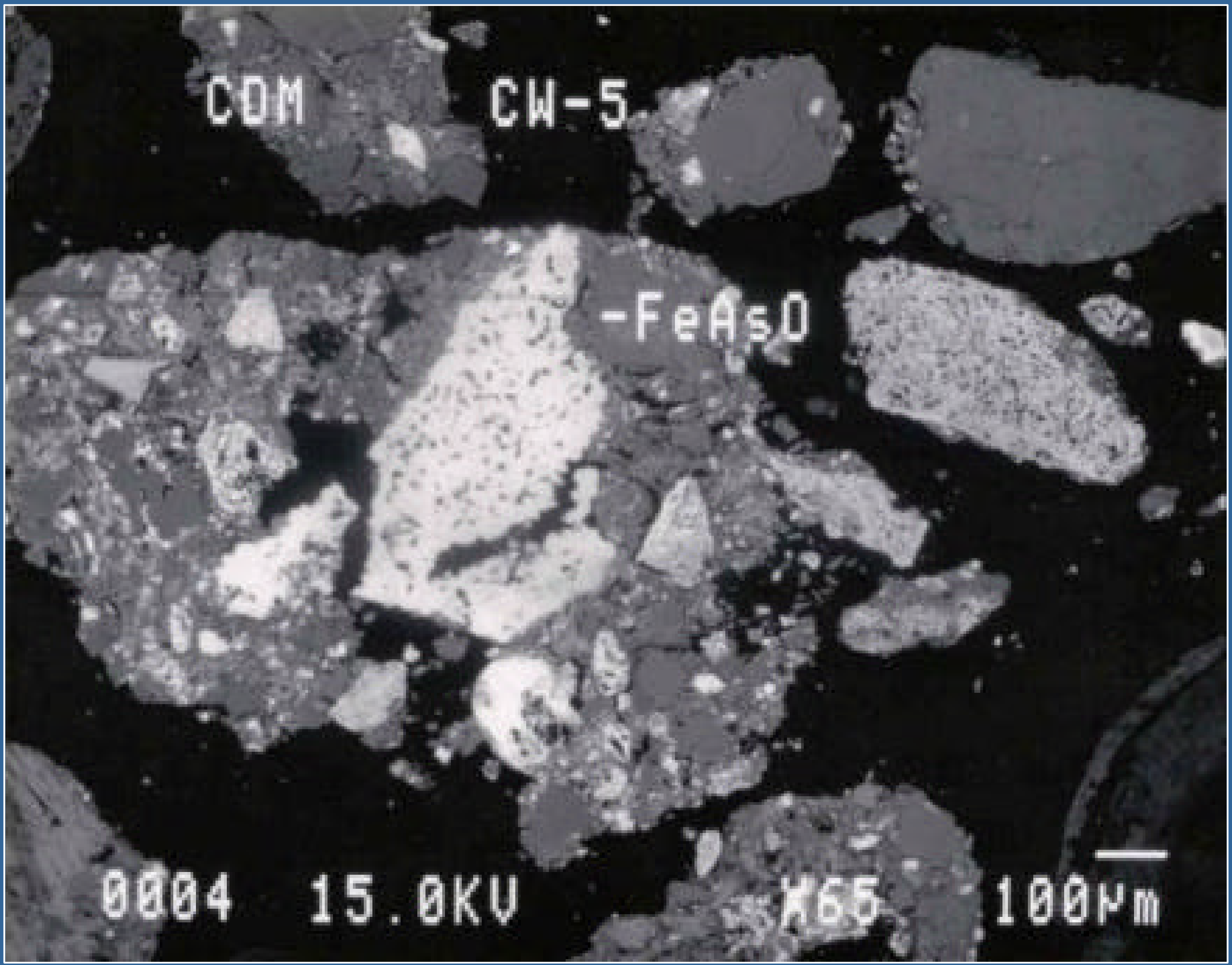
Calcine Waste – Arsenopyrite (arsenian pyrite)/Scorodite



Calcine Waste – Iron Oxyhydroxides



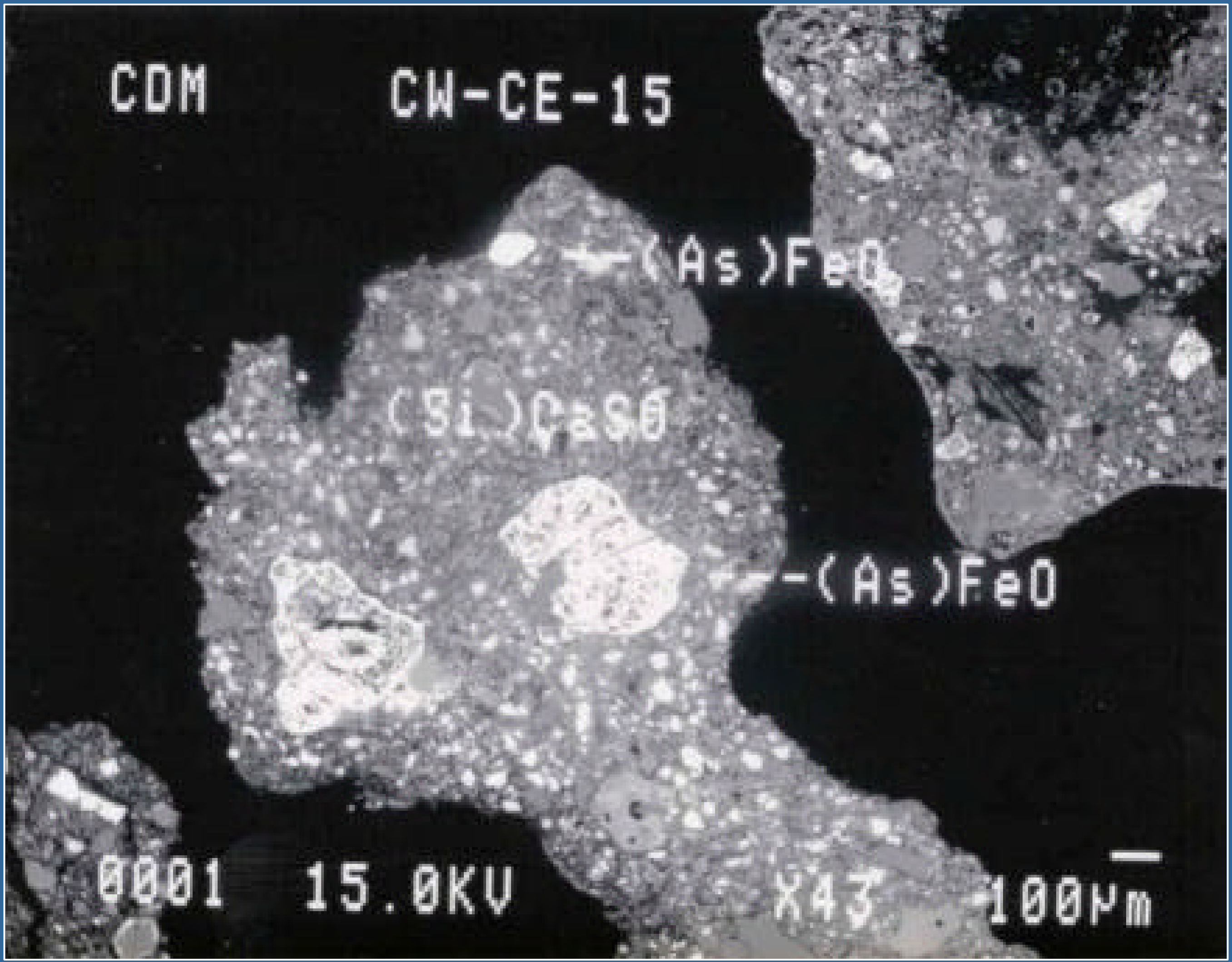
Calcine Waste – Scorodite/Gypsum



S/S Agents

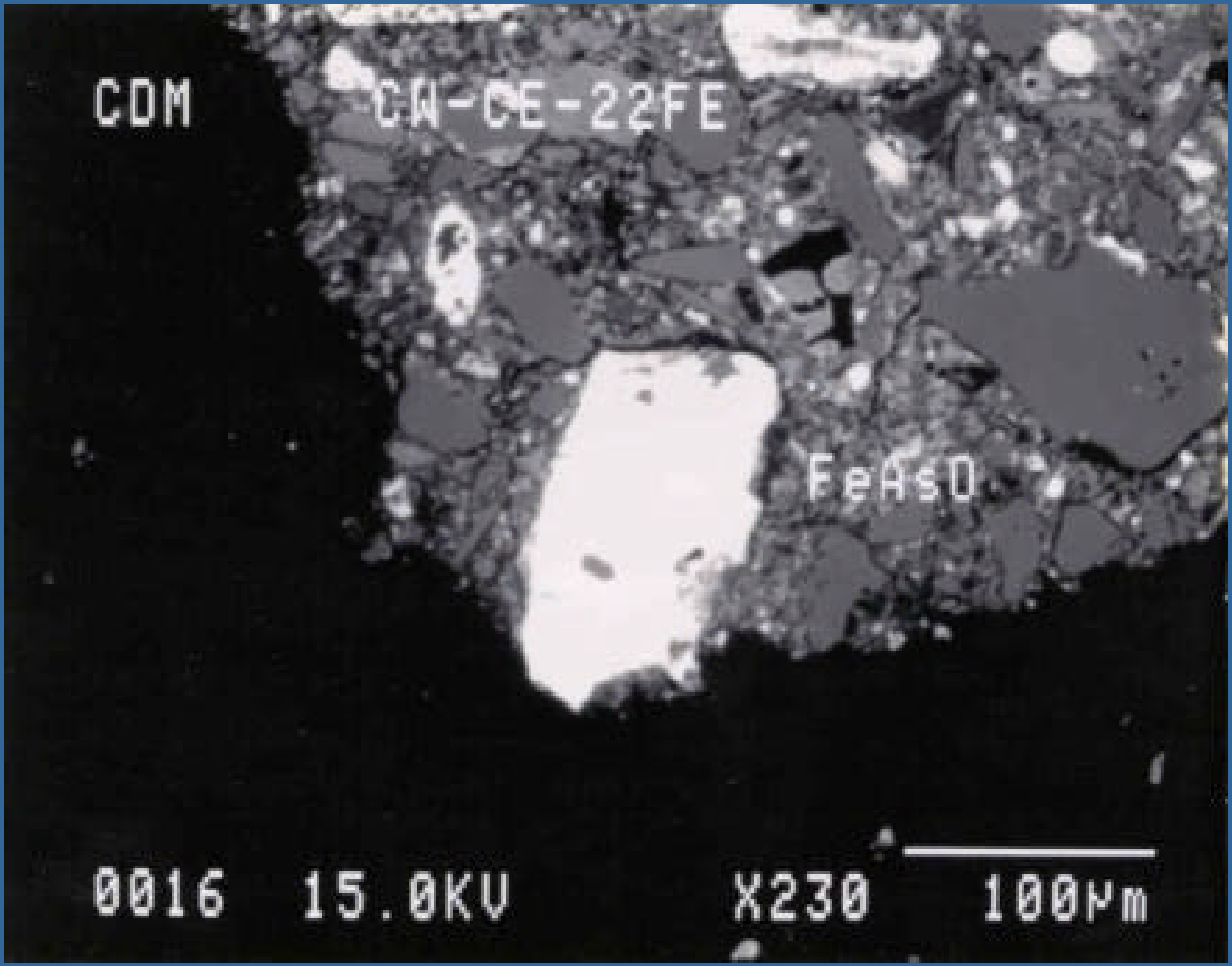
- Cement and Lime Kiln Dust
- Class F Fly Ash
- Type I-II Portland Cement
  - 9%
  - 15%
- Ferrous Sulfate
- Solucorp Molecular Binding Compound

Calcine Waste
15% Cement

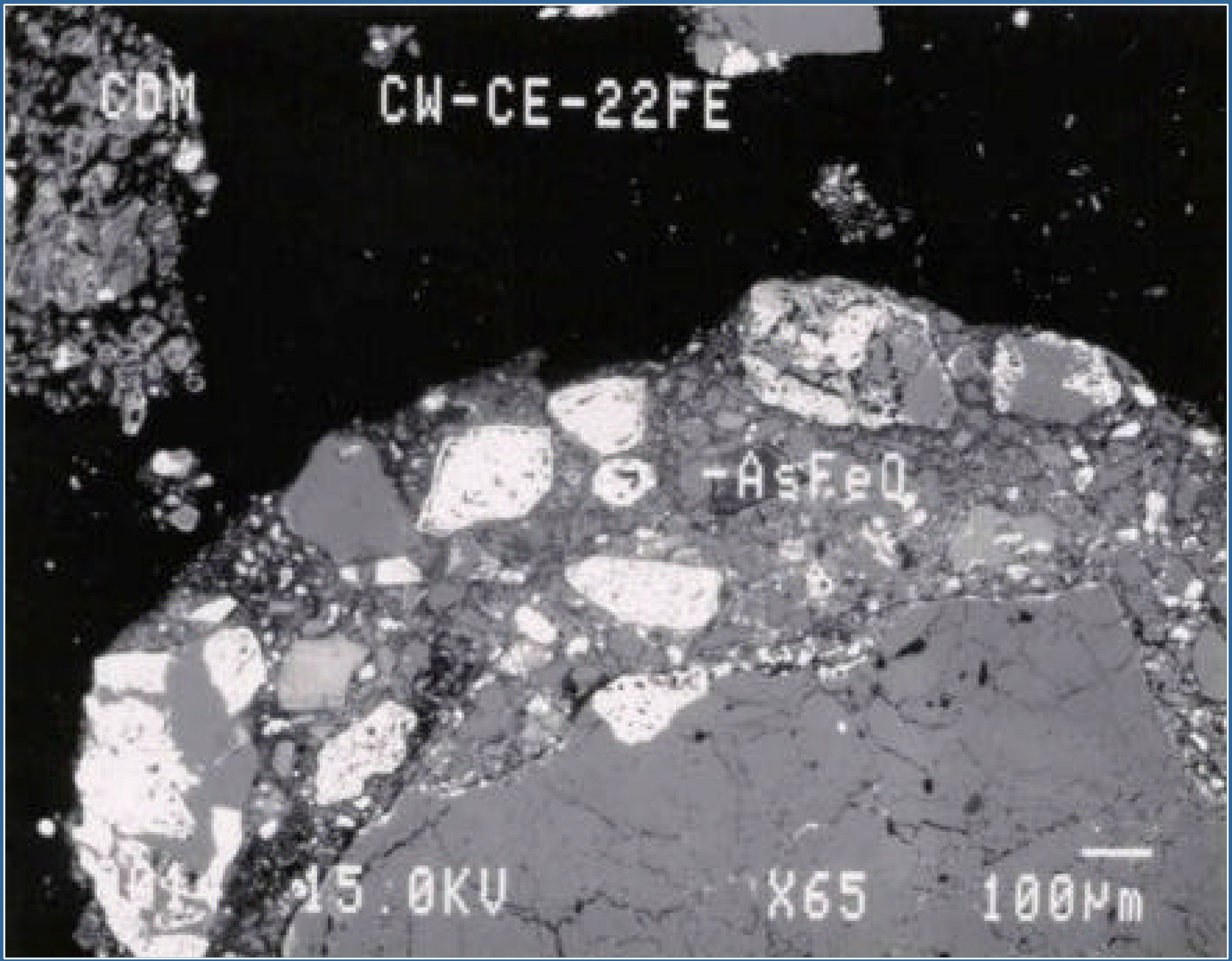


Calcine Waste
15% Cement

Calcine Waste
15% Cement/$FeSO_4$



Calcine Waste
15% Cement/FeSO$_4$



Calcine Waste
15% Cement/$FeSO_4$